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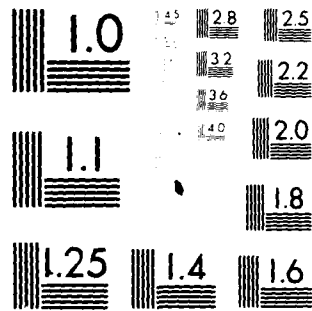
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"SUPER HYDRIDES"

FINAL REPORT

HERBERT C. BROWN  
PRINCIPAL INVESTIGATOR

1 February 1979 to 31 January 1982

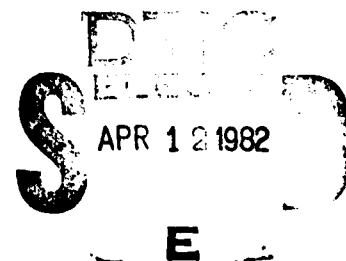
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  see next page		

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## 20. ABSTRACT

The unusual reactivity of lithium triethylborohydride (Super Hydride) encouraged us to examine the selective reduction properties of a number of new reducing agents. Lithium trialkylborohydrides ( $\text{LiR}_3\text{BH}$ ) reduce most of the organic functional groups rapidly. On the other hand, lithium borohydride ( $\text{LiBH}_4$ ) is a mild reducing agent. In order to develop new reagents which can be used for specific reductions, the alkali metal dialkylborohydrides ( $\text{MR}_2\text{BH}_2$ ) and alkylborohydrides ( $\text{MRBH}_3$ ) were prepared successfully. Although the full potentialities of these reagents are yet to be explored, preliminary studies have shown very encouraging results.

We have developed new improved methods for the reduction of esters, nitriles, and amides with the convenient and readily available reagent, borane-dimethyl sulfide ( $\text{BH}_3 \cdot \text{SMe}_2$ , BMS). These developments have simplified the reduction of such functional groups. Lithium borohydride, a relatively expensive, but useful, reducing agent, has been prepared from sodium borohydride. This method is generally applicable for the preparation of various borohydrides.

The reduction of esters by lithium borohydride is catalyzed by trialkylboranes, dialkylborinates and even by methyl borate. Such catalyzed reactions proceed rapidly. Similarly, esters catalyze the hydroboration of alkenes with lithium borohydride.

Potassium triisopropoxyborohydride is an extremely mild reducing agent, and is valuable for the stepwise hydroboration reactions. However, the impurity (15-25%) present in the commercial sample greatly limits the application of this reagent. We have solved this problem by employing a new method for the preparation of this reagent in excellent purity.

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## INTRODUCTION

Various hydride reducing agents have evolved following the discovery by the author (with Professor Schlesinger), forty-five years ago, that diborane reduces carbonyl groups with exceptional ease. The discovery of sodium borohydride (1942) and lithium aluminum hydride (1945) have revolutionized the procedures used by synthetic organic chemists. The author's major contributions in this area, with the financial assistance from ARO, has led to the discovery of various classes of reducing agents. Consequently, a synthetic chemist can now reduce one organic functional group in the presence of the other by the proper choice of a reagent.

Electrophilic reagents, such as borane and alane, possess distinctly different reducing properties from those of nucleophilic reagents, such as sodium borohydride and lithium aluminum hydride. Investigations in this laboratory have revealed means of enhancing and diminishing electrophilic or nucleophilic properties of these reagents.

The author's discovery of hydroboration in 1956 has made available a variety of alkylboranes, which can be converted to the corresponding borohydrides. Lithium triethylborohydride (Super Hydride) is the most reactive reducing agent. Other alkylborohydrides have been prepared recently. Just as the replacement of hydrogen atoms in lithium borohydride with alkyl groups increases the reactivity of the reagent, substitution with alkoxy groups diminishes the reactivity. Thus, the trialkoxyborohydrides are very mild reducing agents.

It should be pointed out that continued research in this area will make available specific reagents which will enable us to reduce any specific functional group in the presence of any other functional group. With our

2.

increasing understanding in this area, it is hoped that we shall be in a position to design reducing agents to perform desired reductions--as specific as the enzymes designed by nature. At the same time our exploration of new compounds in this area of chemistry uncovers new high energy materials that could be of importance to defense requirements.



## LIST OF PARTICIPATING PERSONS

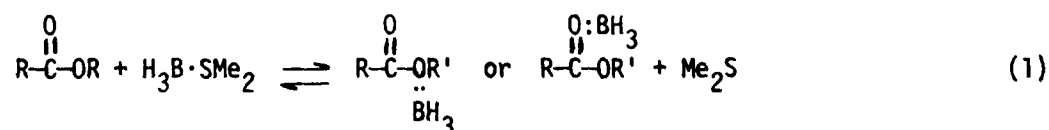
<u>Name*</u>	<u>Period of Appointment</u>
S. Krishnamurthy	2/1/79 - 4/25/79
Y. M. Choi	2/1/79 - 5/31/81
C. P. Mathew	2/1/79 - 10/31/79
S. Narasimhan	4/1/79 - present
K. Muralidhar	8/15/79 - 8/15/81
B. Nazer	9/1/80 - present
V. Somayaji	8/15/81 - present

\*All persons listed are Postdoctoral Research Associates.

## PROBLEMS STUDIED AND THE RESULTS AND CONCLUSIONS REACHED

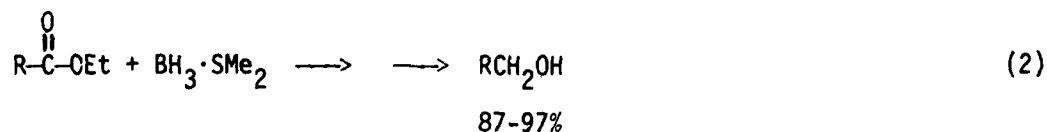
1. A Simple Technique to Achieve an Enhanced Rate of Reduction of Representative Organic Compounds by Borane-Dimethyl Sulfide

Borane-dimethyl sulfide (BMS) is a neat, stable liquid and hence has several advantages over other borane reagents. However, application of BMS for selective reduction of esters, nitriles and amides is limited since the reactions are often quite slow. In a typical study of the rate of reduction of ethyl benzoate using BMS, we noted that the reaction was 67% complete in 0.25 h, but then required more than 8 h to go to essential completion (98%). It appeared that the reaction was fastest with uncomplexed diborane, slower with borane-THF, and slowest with BMS. Evidently, the more tightly coordinated the borane, the slower the reduction. This suggested that the reduction probably proceeds through a transfer of borane from its complexes to the ester group.



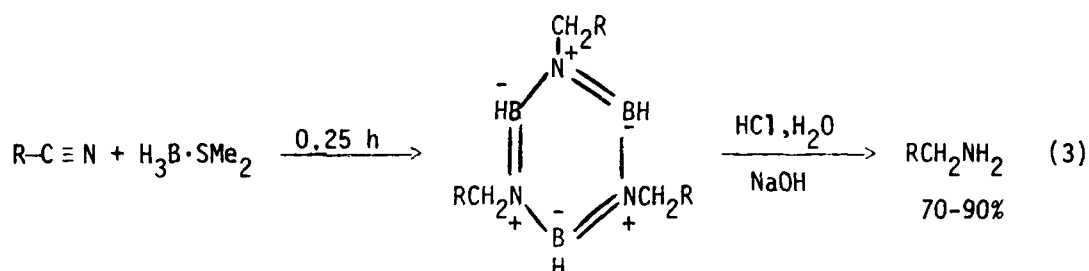
On this basis, the decrease in the rate of reduction of ethyl benzoate by BMS as the reaction proceeds could be attributed to a combination of two factors. First, the accumulation of  $\text{SMe}_2$  in the reaction mixture would repress the transfer of borane to the ester group to give the desired intermediate (eq 1). Second, the accumulation of dimethyl sulfide, bp  $38^\circ\text{C}$ , would reduce the temperature of the refluxing reaction mixture (THF, bp  $67^\circ\text{C}$ ). It appeared that a simple distillation from the reaction mixture of dimethyl sulfide, as it was liberated, would overcome the difficulty. Indeed, that proved to be the case. With distillation, the reaction was essentially complete (100%) in 1 h.

Based on the above observation, a new improved procedure has been developed for the reduction by BMS of representative organic functional groups, such as esters, nitriles and amides. The procedure involves addition of BMS to the substrate in refluxing tetrahydrofuran, allowing the liberated dimethyl sulfide to distill off during the reaction. Stoichiometric studies established the minimum amount of BMS required for the complete reduction of these functional groups. Thus, esters require two equivalents of hydride ( $\text{H}-\text{B}$ ) for the reduction of  $\text{>C=O}$  to  $\text{>CH}_2$ . Employing this stoichiometry, the reduction of a number of esters was achieved quite rapidly, producing alcohols in excellent yields.

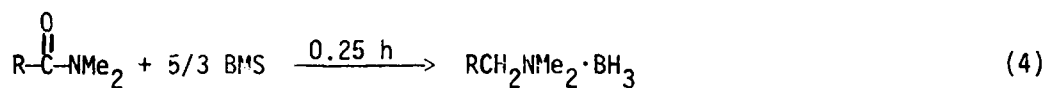


Nitriles require three equivalents of hydride (one borane unit per nitrile) and are reduced rapidly in 0.25 h to the corresponding borazine complex, readily

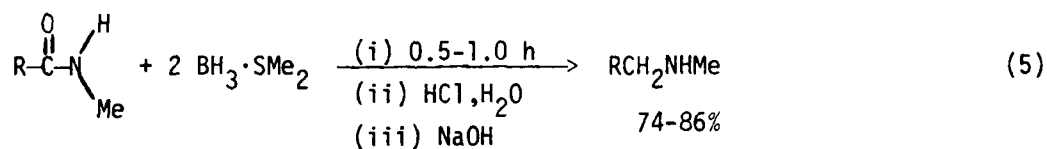
hydrolyzed to the corresponding amines.



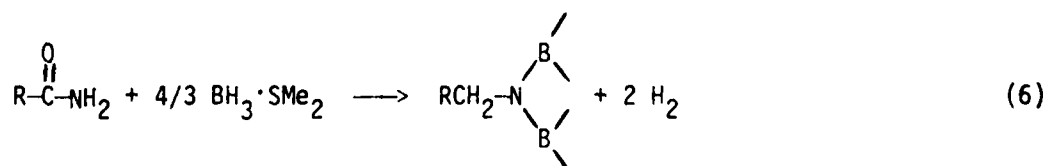
On the other hand, amides require different equivalents of hydride, depending on the particular type of amide undergoing reduction. Thus, tertiary amides require five equivalents of hydride and form the amine-borane adducts in 0.25 h.



Hydrolysis of the amine-borane complex produces amines in yields of 80-90%. Secondary amides liberate hydrogen prior to forming the amine-borane complex, utilizing six equivalents of hydride in 0.25 h to 1.0 h.

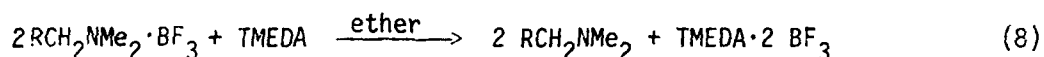
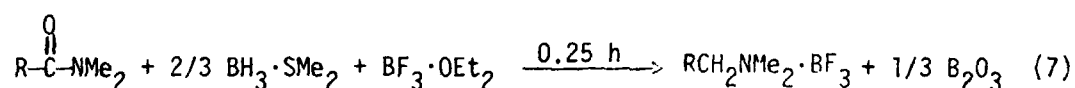


However, primary amides require only four equivalents of hydride, two for hydrogen liberation and two for reduction, producing in 1.0 to 2.0 h the amine dibora derivatives, which are sufficiently weakly basic as not to complex with BMS.



Treatment of the dibora derivative with hydrogen chloride in ether produces the corresponding amine-HCl in excellent yields.

In the reduction of secondary and tertiary amides, excess BMS used for complex formation is being wasted during hydrolysis. Hence, a simple procedure has been described for the reduction of secondary and tertiary amides using decreased amounts of BMS in the presence of boron trifluoride etherate.

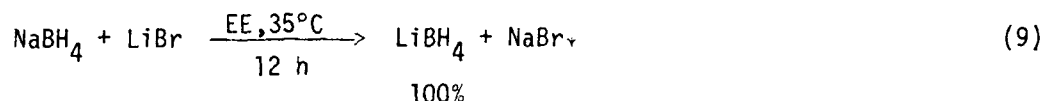


Unlike lithium aluminum hydride or super hydride, the tendency for C-N bond cleavage to produce the alcohol is completely absent in these reductions using BMS. The reagent permits the presence of many common substituents, such as nitro, chloro, methoxy, etc. The reaction is not significantly susceptible to electronic and steric effects. Simple procedures have been developed for isolating the products.

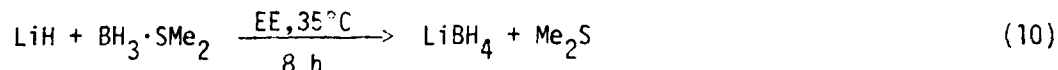
## 2. Modified Convenient Procedure for the Preparation of Lithium Borohydride from Sodium Borohydride and Borane-Dimethyl Sulfide in Simple Ether Solvents

The preparation of  $\text{LiBH}_4$  in various ether solvents from readily available reagents,  $\text{NaBH}_4$  and lithium halide, has been studied. The reactivity of lithium halides towards the metathesis reaction generally follows the order  $\text{LiBr} > \text{LiI} > \text{LiCl}$ . The heterogeneous reactions proceed satisfactorily with vigorous magnetic stirring. However, attempts to increase the scale of the preparations utilizing mechanical stirrers resulted in incomplete reactions and decreased yield. On the other hand, when the heterogeneous mixture was stirred with mechanical stirrers fitted with Teflon paddles and a mass of glass beads,

the rate of the reaction increased considerably, producing quantitative yields of  $\text{LiBH}_4$  in greatly decreased reaction times. The ease of conversion of  $\text{NaBH}_4$  into  $\text{LiBH}_4$  in various solvents follows the order isopropylamine > 1,3-dioxolane > monoglyme > tetrahydrofuran  $\approx$  ether. The isolation of solvent-free  $\text{LiBH}_4$  from the various solvates was attempted under different conditions. In most cases, normal distillation at  $100^\circ\text{C}$  or  $150^\circ\text{C}$  produced a strong 1:1 solvate,  $\text{LiBH}_4 \cdot \text{solvent}$ . Only in the case of ethyl ether is the solvent of solvation readily removed at  $100^\circ\text{C}$  at atmospheric pressure. In the other cases, both higher temperatures, up to  $150^\circ\text{C}$ , and lower pressures, down to 0.1 mm, are required to produce the unsolvated material. Thus the ease of isolating unsolvated  $\text{LiBH}_4$  is ethyl ether > IPA > THF > 1,3-D  $\approx$  MG. Consequently, ethyl ether is the medium of choice for the preparation of  $\text{LiBH}_4$  by the metathesis of  $\text{NaBH}_4$  and  $\text{LiBr}$ .



$\text{LiBH}_4$  can also be conveniently prepared by the reaction of  $\text{LiH}$  with  $\text{BH}_3$  in ethyl ether. Dimethyl sulfide is readily removed, along with ethyl ether of solvation, at  $100^\circ\text{C}$  (atmospheric pressure).



### 3. Effect of Cation and Solvent on the Reactivity of Saline Borohydrides for Reduction of Carboxylic Esters. Improved Procedures for the Conversion of Esters to Alcohols by Metal Borohydrides

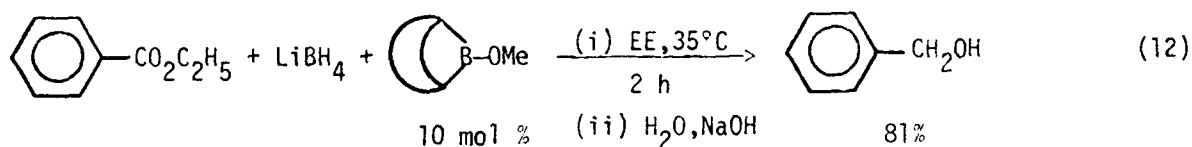
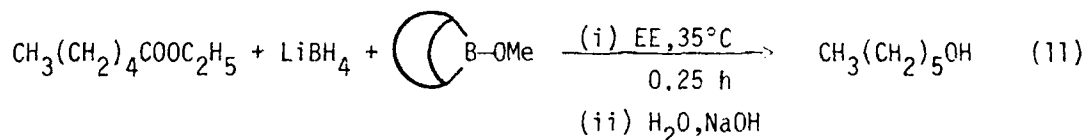
A comparative study of the relative reactivity of saline borohydrides ( $\text{Li}$ ,  $\text{Na}$ ,  $\text{Ca}$ ) for the reduction of carboxylic esters has been made in selected

solvents (ether, THF, diglyme, 2-propanol, and ethanol) at 25°C. In ether solvents the reactivity follows the trend  $\text{LiBH}_4 > \text{Ca}(\text{BH}_4)_2 > \text{NaBH}_4$ . On the other hand, in alcohol solvents the order of reactivity is  $\text{Ca}(\text{BH}_4)_2 > \text{LiBH}_4 > \text{NaBH}_4$ . The reactivities of  $\text{LiBH}_4$  in ethyl ether and THF, of  $\text{Ca}(\text{BH}_4)_2$  in THF and 2-propanol and of  $\text{NaBH}_4$  in ethanol proved to be promising for the reduction of esters. However, alcohol solvents are not useful for reductions at elevated temperatures because the decomposition of the reagents becomes competitive with the reduction. A convenient synthetic procedure has been developed for the rapid conversion of esters to alcohols using  $\text{LiBH}_4$  in ethyl ether and THF and  $\text{Ca}(\text{BH}_4)_2$  in THF, utilizing essentially stoichiometric amounts of the reagents. The procedure involves adding toluene to the reaction mixture, bringing the temperature to 100°C, allowing solvent to distill off. Following completion of the reaction, toluene is readily removed under vacuum and the reaction product hydrolyzed. The reductions were generally complete in 0.5-2.0 h and high yields of alcohols (73-96%) were isolated. A number of ester derivatives, including compounds containing nitro, halo, cyano, alkoxy groups, diester and lactones were reduced by this procedure. The reagents are highly selective, permitting the rapid reduction of the ester group in the presence of many substituents. However, unsaturated esters undergo simultaneous hydroboration when reduced by this procedure.

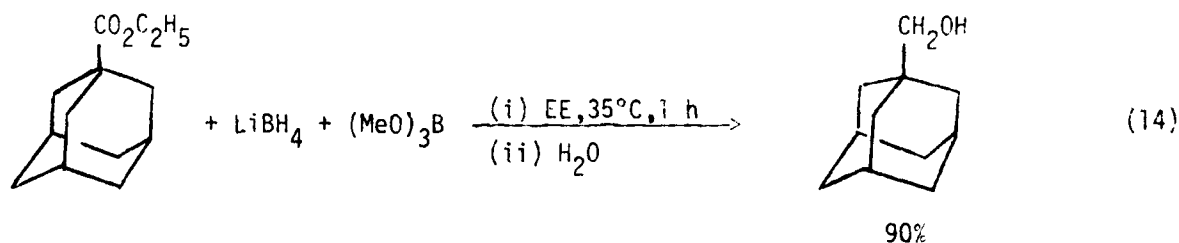
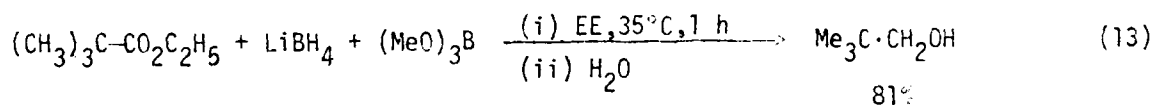
#### 4. New Powerful Catalysts for the Reduction of Esters by Lithium Borohydride

The important application of  $\text{LiBH}_4$  is the reduction of esters, especially in the presence of other reducible groups. We found that the reduction of esters proceeds smoothly, but relatively slowly. The reaction is considerably faster in ethyl ether than in THF. However, even in refluxing EE, typical esters, such as ethyl caproate, required 5 h and ethyl benzoate ~ 24 h to go to

completion. On the other hand, lithium triethylborohydride and lithium 9-boratabicyclo[3.3.1]nonane reduce esters very rapidly, the reaction being complete within 5 min. We then examined the possibility that small quantities of these compounds could catalyze the reduction of esters by lithium borohydride. Indeed, we observed a remarkable enhancement of the rate in the presence of 10 mole percent of  $\text{LiEt}_3\text{BH}$  or  $\text{LiH}\cdot 9\text{-BBN}$ . It appeared that the reduction of esters by  $\text{LiEt}_3\text{BH}$  or  $\text{LiH}\cdot 9\text{-BBN}$  must produce species capable of enhancing the reaction, being regenerated under the reaction conditions. We also found that the corresponding Lewis acid, *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-OMe-9-BBN) permits the rapid and quantitative reduction of esters by  $\text{LiBH}_4$ .

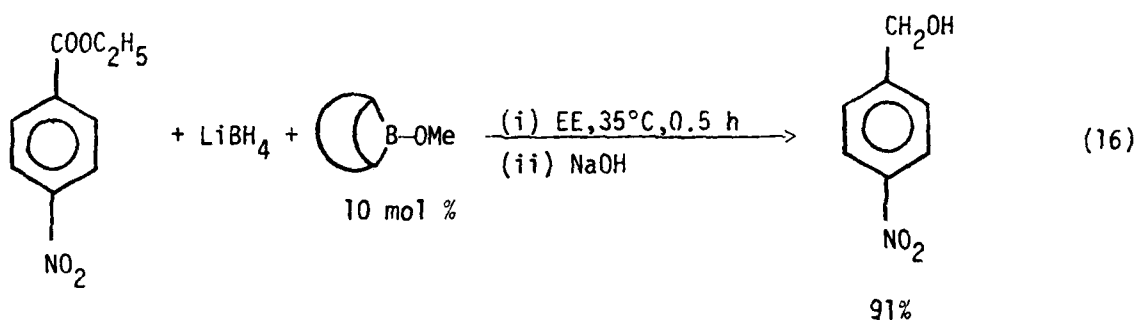
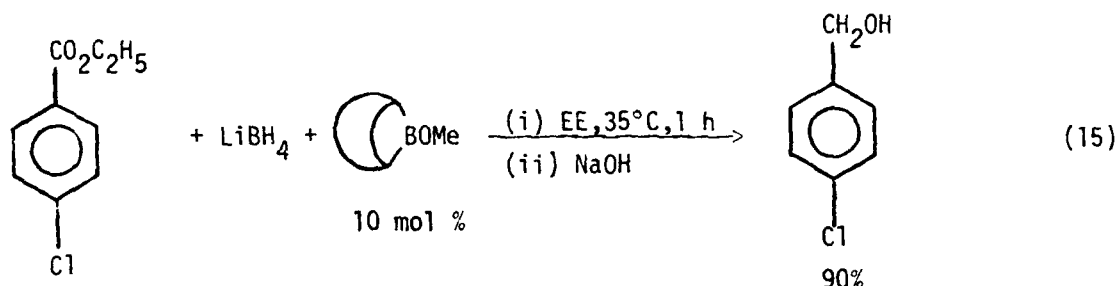


Even sterically hindered esters are reduced easily when trimethylborate is used as a catalyst.



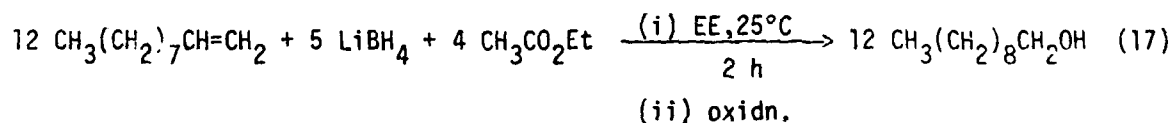
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The catalysts, *B*-OMe-9-BBN and (MeO)<sub>3</sub>B can be easily removed from the reaction product by extracting with 3 *N* sodium hydroxide solution. Selective reduction of esters in the presence of chloro and nitro groups is also achieved by this method.



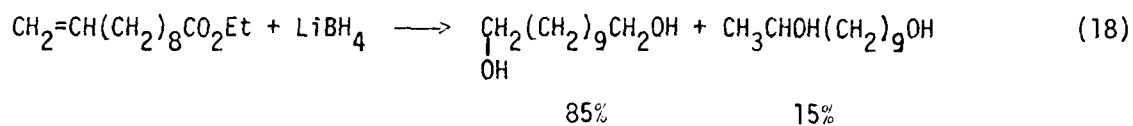
##### 5. Controlled Hydroboration of Alkenes by Lithium Borohydride Induced by the Reduction of Carboxylic Esters

Alkenes which are normally inert to lithium borohydride are rapidly hydroborated in the presence of carboxylic esters in ether at 25°C, to provide dialkylborinates. Oxidation of the reaction product produces alcohols in quantitative yields with a selectivity similar to that of borane.

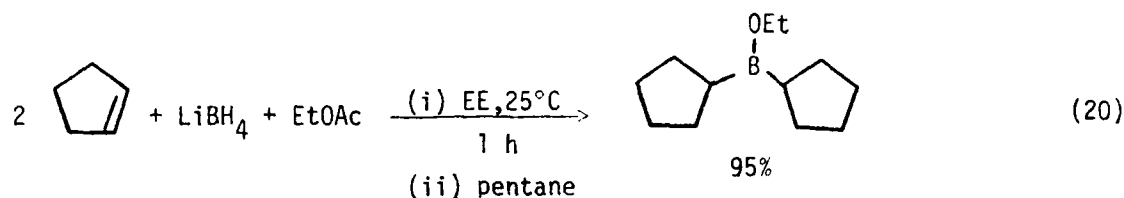
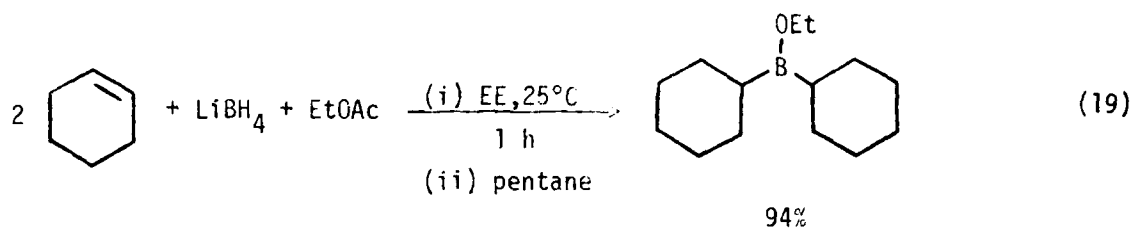




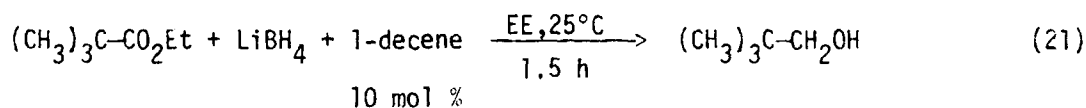
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Cyclic olefins produce dialkylborinates in very good yields.



At the same time, catalytic amounts of alkenes markedly enhance the rate of reduction of esters by lithium borohydride.

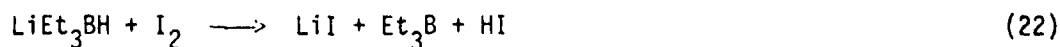


A reasonable explanation has been offered to account for these unexpected reactions.

Further work is in progress regarding the controlled hydroboration of alkynes and other unsaturated systems by  $\text{LiBH}_4$  in the presence of esters.

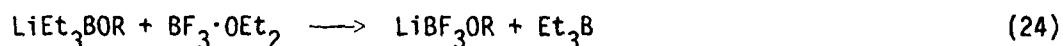
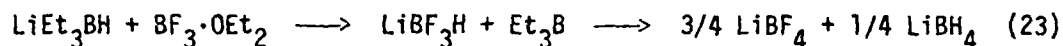
#### 6. Procedure for the Estimation of Super Hydride by Iodometry

Lithium triethylborohydride reacts with  $\text{I}_2$  in toluene as follows:



This reaction has been made use of in estimating super hydride quantitatively.

However, in the presence of a substrate such as ketone, aldehyde, etc., difficulties were encountered due to the reaction of  $\text{LiEt}_3\text{BOR}$  with iodine. The problem was solved by the addition of  $\text{BF}_3 \cdot \text{OEt}_2$  which reacts with  $\text{LiEt}_3\text{BH}$  and  $\text{LiEt}_3\text{BOR}$  as follows.



This permitted the estimation of hydride content without any side-reaction resulting in the consumption of iodine.

Following this procedure, the kinetics of reduction of epoxides by super hydride has been studied. The reaction follows a total second order kinetics. The rate of reaction depends on the substrate structure. *cis*-Epoxides react much faster than the *trans*-epoxides. The rate is very much susceptible to steric factors. The reaction exhibits a kinetic isotope effect of  $\sim 1.5$ . A suitable mechanism has been proposed for the reduction of epoxides by  $\text{LiEt}_3\text{BH}$ .

#### 7. Preparation of Dialkyl- and Monoalkylborohydrides

The reactivity of  $\text{MH}$  ( $\text{M}$  is  $\text{Li}$ ,  $\text{Na}$ , or  $\text{K}$ ) toward different mono- and dialkylboranes was studied (eq 25, 26).



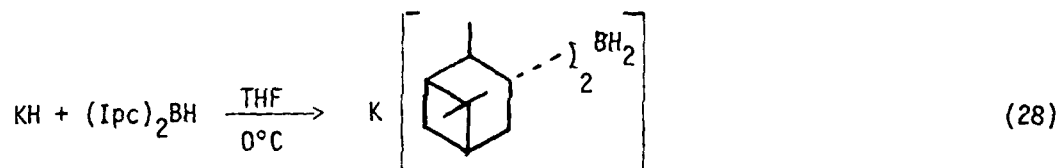
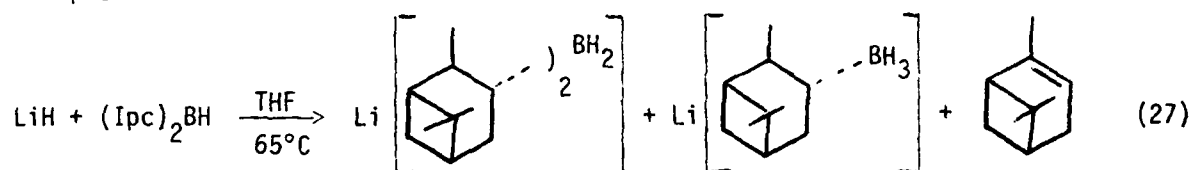
Five representative organoboranes, 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane ( $\text{Chx}_2\text{BH}$ ), diisamylborane ( $\text{Sia}_2\text{BH}$ ), di- and monoisopinocampheylborane ( $\text{Ipc}_2\text{BH}$ ,  $\text{IpcBH}_2$ ), were studied.

It was found that increasing the size of the alkyl group on boron retards the reactivity of organoboranes toward alkali hydrides. Thus, the reactivities

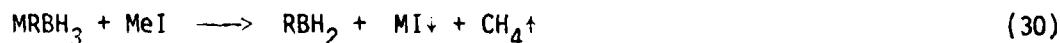
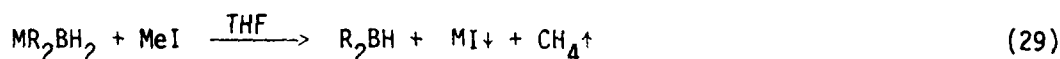
were in the order: 9-BBN > (Chx)<sub>2</sub>BH > Sia<sub>2</sub>BH > (Ipc)<sub>2</sub>BH.

Among alkali hydrides studied, the reactivity decreases in the order KH > NaH > LiH. This trend of reactivity is similar to that observed for trialkylboranes.

The lower reactivity of LiH can be overcome by increasing the temperature. Unfortunately, using a higher temperature for the reaction in some cases resulted in the disproportionation of the borohydride product while the use of KH solved the problem.



The solutions of mono- and dialkylborohydrides, protected from moisture and heat, are stable at room temperature. The corresponding mono- and dialkylboranes can be regenerated by the addition of methyl iodide.



#### 8. Preparation of Trialkylborohydrides from Trialkylboranes and Lithium Aluminum Hydride

It is known that trialkylboranes accept one equivalent of hydride from LAH in ether solvents. The remaining alane, AlH<sub>3</sub>, can be separated as an adduct with TED.

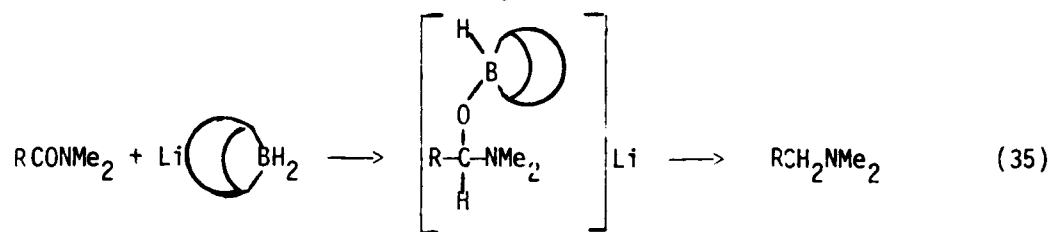


Carboxylic acids instantly evolve one equivalent of hydrogen from the corresponding lithium salts. Further hydride uptake is extremely slow. This is important in that the reagent may be used to reduce multifunctional organic compounds containing carboxylic acid groups.

Acid chlorides react rapidly, utilizing theoretical quantities of hydride, giving alcohols.

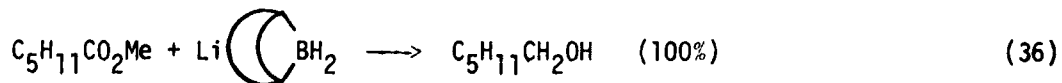


Primary amides react evolving two equivalents of hydrogen instantaneously. There is no further hydride uptake. On the other hand, secondary amides liberate hydrogen only slowly but undergo sluggish reduction, consuming about 1.2 equivalents of hydride in 24 h. Tertiary amides are reduced to the corresponding amines. By suitably manipulating the reaction conditions, it is possible to obtain a quantitative cleavage of C-O bond.

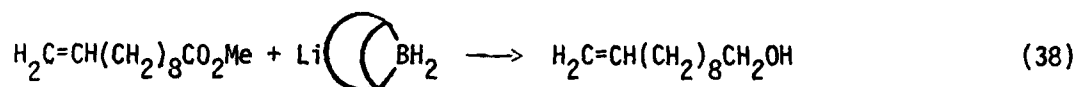
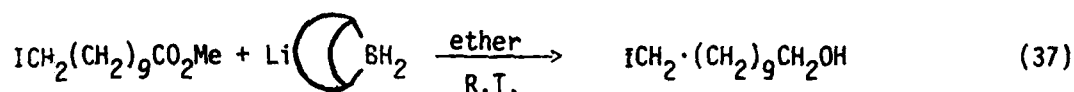


Epoxides are reduced quantitatively in less than 1 h with an uptake of one equivalent of hydride. However, the case of alkyl halides is different. While iodides are reduced, chlorides are not. Bromides react very slowly.

Esters are reduced very rapidly with the consumption of two equivalents of hydride per mole, giving essentially quantitative yields of alcohols.

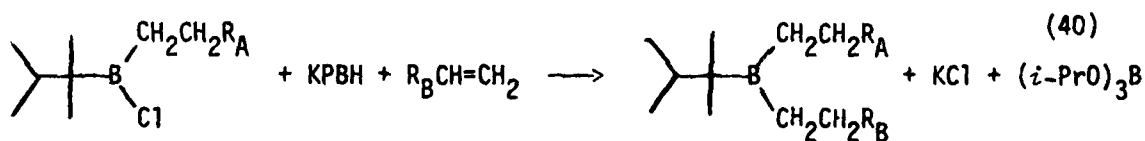
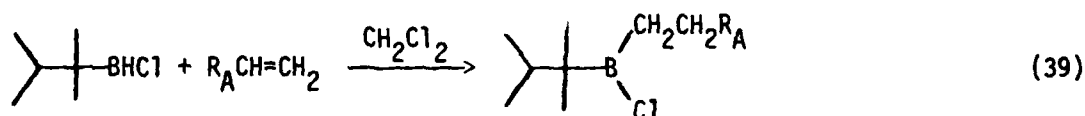


Tosylates are unaffected by this reagent as opposed to lithium triethylborohydride, which reduces the tosylates to the alkanes and alkenes. Benzonitrile reacts sluggishly, consuming only 1.7 equivalents of hydride per mole, resulting in a mixture of amine and aldehyde. The following two reactions are typical of the applications of lithium 9-boratabicyclo[3.3.1]nonane.



#### 10. Preparation of Pure Potassium Triisopropoxyborohydride (KPBH)

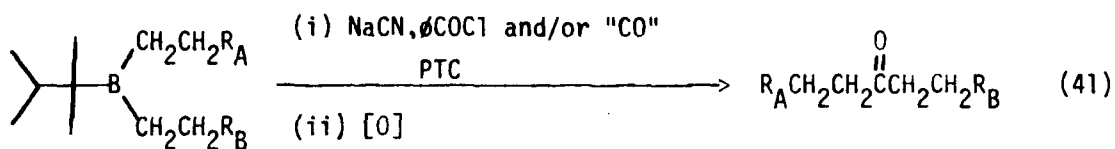
Preparation of 98-99% pure KPBH was achieved. The reagent was prepared by refluxing triisopropoxyborane  $(i\text{-PrO})_3\text{B}$  over 50% excess KH in THF for 24 h. Unlike the commercial samples of the reagent, this 98-99% reagent showed an excellent application for stepwise hydroboration of  $\text{ThxBRCI}$  in the presence of a second olefin.



On the other hand, the use of commercial KPBH with 20-40% impurity [*i.e.*,  $(i\text{-PrO})_4\text{B}$ ] resulted in the formation of  $\text{ThxB}(i\text{-PrO})\text{R}_A$ , which is ineffective toward second hydroboration.

The use of a purer reagent in stepwise hydroboration with  $\text{ThxBHCl}$ , followed by cyanidation or carbonylation to synthesize unsymmetrical ketones, is

under study. Different types of ketones with high purity and yields were prepared.



#### 11. Thexylchloroborane-Methyl Sulfide as a Selective Reducing Agent

Thexylchloroborane, readily prepared from monochloroborane and 2,3-dimethyl-2-butene in methylene chloride, offers considerable promise as a selective reducing agent. Various classes of compounds were treated with excess reagent in methylene chloride at 0°C. Alcohols and thiols liberate hydrogen rapidly and quantitatively. Aldehydes and ketones are reduced rapidly and quantitatively to the corresponding alcohols. Carboxylic acids liberate hydrogen immediately and then are reduced to the corresponding aldehydes.

Acid chlorides and acid anhydrides react only slowly with the reagent, and esters do not undergo reduction under standard conditions. Pyridine forms an addition compound, but does not undergo reduction. On the other hand, sulfoxides are rapidly reduced to the corresponding sulfides. Consequently, this reagent reveals interesting differences from either borane or other borane derivatives, such as disiamylborane or 9-BBN.

#### 12. Tri-*tert*-Butoxyborohydride, K(*tert*-BuO)<sub>3</sub>BH

Preparation of pure K(*tert*-BuO)<sub>3</sub>BH was accomplished for the first time. The stereoselectivity of this reagent toward different cyclic ketones is under study. Preliminary results are very promising. For example, 2-methylcyclohexanone was reduced at 0° to the corresponding *cis*,*trans* alcohols in a ratio of 92:8. The reagent is stable at room temperature and no disproportionation was observed,

## LIST OF PUBLICATIONS

This is in continuation of the list submitted with the last Final Report (Grant No. DAAG-29-76-G-0218 covering the period 5/1/76-1/30/79). Twenty-five reprints of each of the publications have been sent along with Semi-Annual Reports.

1. Selective Reductions. 25. Remarkably Facile Reductive Opening of Cyclic Ethers by the Lithium Tri-*tert*-butoxyaluminumhydride-Triethylborane Combination  
S. Krishnamurthy and H. C. Brown  
*J. Org. Chem.* 1979, 44, 3678
2. Selective Reductions. 26. Lithium Triethylborohydride as an Exceptionally Powerful and Selective Reducing Agent in Organic Synthesis. Exploration of the Reactions with Selected Organic Compounds Containing Representative Functional Groups  
H. C. Brown, S. C. Kim and S. Krishnamurthy  
*J. Org. Chem.* 1980, 45, 1
3. Selective Reductions. 27. Reaction of Alkyl Halides with Representative Complex Metal Hydrides and Metal Hydrides. Comparison of Various Hydride Reducing Agents  
S. Krishnamurthy and H. C. Brown  
*J. Org. Chem.* 1980, 45, 849
4. Addition Compounds of Alkali Metal Hydrides. XVIII. Reaction of Trialkylboranes with *t*-Butyllithium. A General, Convenient Method for the Preparation of Lithium Trialkylborohydrides  
H. C. Brown, G. W. Kramer, J. L. Hubbard and S. Krishnamurthy  
*J. Organometal. Chem.* 1980, 188, 1
5. Addition Compounds of Alkali Metal Hydrides. 20. Reaction of Representative Mono- and Dialkylboranes with Saline Hydrides to Form the Corresponding Alkylborohydrides  
H. C. Brown, B. Singaram and C. P. Mathew  
*J. Org. Chem.* 1981, 46, 2712
6. Improved Procedure for Borane-Methyl Sulfide Reduction of Carboxylic Esters  
H. C. Brown and Y. M. Choi  
*Synthesis* 1981, 439
7. Improved Procedure for Borane-Methyl Sulfide Reduction of Primary Amides to Amines  
H. C. Brown, S. Narasimhan and Y. M. Choi  
*Synthesis* 1981, 441
8. Improved Procedure for Borane-Methyl Sulfide Reduction of Nitriles  
H. C. Brown, Y. M. Choi and S. Narasimhan  
*Synthesis* 1981, 605



9. Addition Compounds of Alkali Metal Hydrides. 21. Rapid Reaction of Dialkyl- and Monoalkylboranes with Lithium Aluminum Hydride in the Presence of Triethylenediamine. A Facile and Quantitative Synthesis of Lithium Dialkyl- and Monoalkylborohydrides  
H. C. Brown, B. Singaram and C. P. Mathew  
*J. Org. Chem.* 1981, 46, 4541
10. Simple Procedure for the Conversion of Sodium Borohydride into Lithium Borohydride in Simple Ether Solvents  
H. C. Brown, Y. M. Choi and S. Narasimhan  
*Inorg. Chem.* 1981, 20, 4454
11. Improved Procedure for Borane-Dimethyl Sulfide Reduction of Tertiary and Secondary Amides in the Presence of Boron Trifluoride Etherate  
H. C. Brown, S. Narasimhan and Y. M. Choi  
*Synthesis* 1981, 996
12. Selective Reductions. 28. The Fast Reaction of Lithium Aluminum Hydride with Alkyl Halides in Tetrahydrofuran. A Reappraisal of the Scope of the Reaction  
S. Krishnamurthy and H. C. Brown  
*J. Org. Chem.* 1982, 47, 276

